

## Structural, Morphological and Optical Properties of Polystyrene/ Silver Nanowire Composites

P. Ramya<sup>1</sup>, L. Priya<sup>2\*</sup>

<sup>1</sup>Department of Physics, CPGS, Jain University, Jayanagar 3<sup>rd</sup> Block, Bangalore, Karnataka, India.

<sup>2\*</sup>Department of Physics, LRG Government Arts College for Women, Tirupur, TN, India.

### Abstract

The optical properties of polymers can be improved by introducing nanomaterials like silver, iron, copper, as these metals exhibits surface plasmon resonance absorption when exposed to visible light. In the present work the influence of silver nanowires (AgNWs) on structure, morphology and optical properties of polystyrene (PS) has been studied. Polystyrene/ AgNW (PSAW) composites is prepared by growing silver nanowires directly into Polystyrene solution. Structural and morphological characteristics have been studied by XRD and FESEM. The silver nanowires exhibit FCC structure in the composite. FESEM of the composites shows uniform distribution of AgNWs in the matrix and they aligned to form a network in the polymer matrix. UV- Vis spectrum shows that the absorption peak in PS has shifted towards the higher wavelengths as the concentration of AgNWs increased in PS. Photoluminescence spectra of the composites excited at 320 nm shows two emission peaks at 410 nm and 440 nm which can be attributed to photoluminescent radioactive recombination of *sp* – band electrons with the holes in the valance *d* band.

Keywords:

### 1. INTRODUCTION

The electrical properties of an insulating polymer can be greatly improved by introducing conducting nano materials like silver, iron (Costa *et al.* 2006). Along with the electrical properties the optical properties of polymers are also improved as these metals exhibits surface plasmon resonance absorption when exposed to visible light. With the introduction of a small amount of these nanostructures a great improvement in the physical properties are also observed. This is due to the large surface area of nanostructures. With controlled shape and size of the nanostructures these materials can be used in various fields (VesnaVodnik *et al.* 2012).

Silver with its interesting properties like anti microbial affect, conductivity, chemical stability, unique optical and thermal properties proved to be the best material to dope into various polymers (Vaia and Maguire, 2007). Polystyrene acts as the polymer to host the nanostructures of silver as it enables good stabilization for Ag nanostructures and can easily be processed in to various devices for different applications such as digital memory devises, surface enhanced Raman scattering, molecular sensing in biomedicine and anti microbial packaging (Koh *et al.* 2009; Pongnop *et al.* 2011; White *et al.* 2011).

In the present work, Polystyrene (PS)/ AgNW (PSAW) composites were synthesized by adding appropriate amount of PS to AgNW suspension in Toluene. PSAW composites were prepared in various

weight percentages of 5, 10, 12, 15 and 20% and were characterized using XRD, FESEM, UV-Vis spectroscopy and Photoluminescent spectroscopy.

### 2. MATERIALS & METHODS

**Materials used:** Silver nitrate (AgNO<sub>3</sub>), Trisodium citrate, Polystyrene (PS) were obtained from SD Fine chemicals Limited. Sodium hydroxide (NaOH), Ethylene and Toluene were purchased from Merc Specialities private limited. Demineralised water has been used for whole synthesis. All the chemicals were used as received.

**Preparation of Silver Nanowires (AgNWs):** AgNWs were synthesized by Seedless, Surfactant less wet chemical method (Caswell *et al.* 2003). The synthesis involves two silver solutions A and B. Beaker A consisted of 100 ml of deionised water, 2 µl of 1M NaOH and 40 µl 0.1M AgNO<sub>3</sub>. This solution was brought to boil with rapid stirring and in this 5 ml of 0.01M trisodium citrate was quickly added. Then the solution was allowed to boil for another 10 min. Concomitantly, Solution B was prepared by adding 150 ml deionised water, 2 µl 1M NaOH and 20 µl 0.1M AgNO<sub>3</sub> and bringing this to boil. Solution B was added to solution A and the mixture was allowed to evaporate till the solution becomes ~75 to 100 ml.

**Preparation of Polystyrene/ AgNW (PSAW):** The prepared AgNW solution has been centrifuged to get AgNW concentration and been mixed with 2 ml of ethanol. Then desired amount of PS has been dissolved

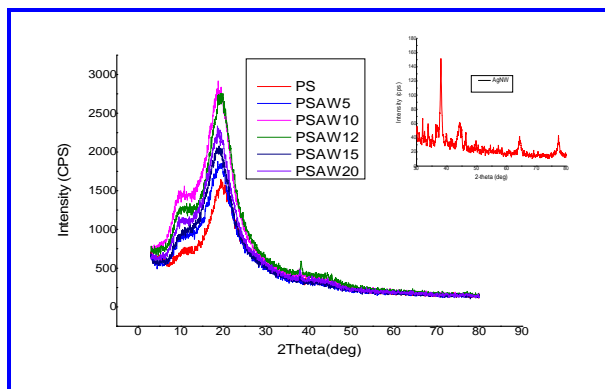
\*L. Priya

email : svl.priya1@gmail.com

in toluene and stirred for about an hour. Then AgNW solution has been dropped to PS/ Toluene mixture and this mixture was allowed to stir for 24 hours in order to mix completely. This solution was poured to a Petri dish and allowed to dry to form a uniform thin film. PSAW composites were prepared in various weight percentages of 5%, 10%, 12%, 15% and 20 % by changing weight / weight ratio of PS and AgNW.

### 3. RESULTS & DISCUSSION

#### X-Ray Diffraction



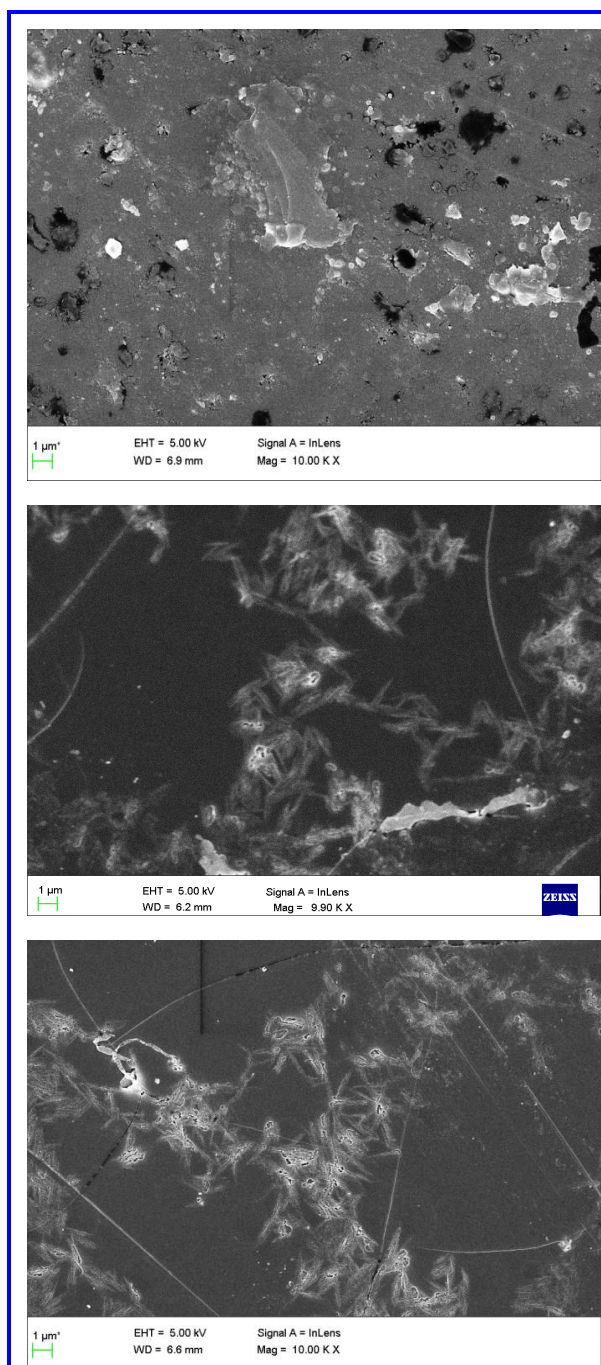
**Fig. 1: XRD of AgNW, PS and PSAW composites**

Structural property of AgNW doped Polystyrene has been determined using powder X- Ray diffraction analysis. Figure 1 shows the XRD of AgNW, pure PS and PSAW composites. XRD of AgNW shows peaks at  $20-38^\circ$ ,  $45^\circ$ ,  $65^\circ$  and  $78^\circ$ . These correspond to (111), (200), (220) and (311) planes respectively of silver as compared with JCPDS silver file No. 04-0783. These peak reflections represent the FCC crystal plane of Silver. Pure PS shows a peak at  $20 \sim 20^\circ$  represents the amorphous phase of PS. The strong reflection at  $20^\circ$  corresponds to (211) plane which is due to the arrangement of phenyl rings in pure polystyrene (De Rosa *et al.* 1991).

In Composites, the peak at  $20-20^\circ$  got intensified by many orders showing influence of doped Ag on the phenyl three fold helical structure of backbone of polystyrene. Ag ordered the phenyl staking because of which intensity of (211) plane has increased. The peaks at  $20-38^\circ$  and  $45^\circ$  represents the FCC crystal structure of silver which is doped in the polymer. As the concentration of Ag increased in the composites the intensity of peak at  $20 = 38^\circ$  has been increased which shows the even distribution of AgNWs in the polymer matrix.

FESEM of pure PS and PSAW composites are shown in the fig. 2. FESEM of PS shows a plain surface with some cracks in some places which may be formed due to the stress applied during the synthesis. FESEM of PSAW samples shows AgNWs dispersed in polystyrene matrix uniformly and the wires are more than a

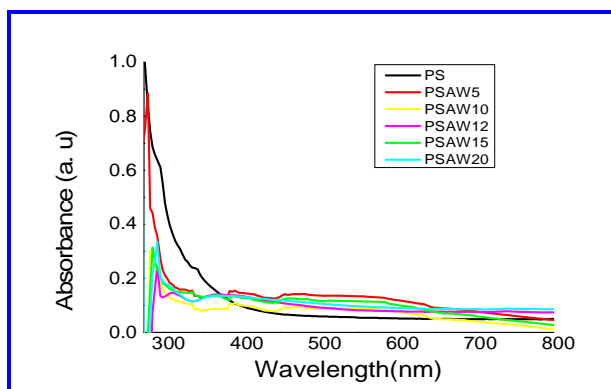
micrometer long which gives a good aspect ratio. FESEM of PSAW5 shows the AgNW network alignment in the PS matrix. The nanowires are attached to one another to form a connecting network. This helped in improving the electrical conductivity of an insulating polymer like polystyrene. In FESEM of PSAW20 it is clearly seen that the number of silver nanowires increased and the alignment of wires has also improved. This increased the conductivity of PSAW20 than that of PSAW5. This uniformly dispersed wires lead to the increased intensity of AgNW peak at (111) with the increased concentration of AgNW in the matrix.



**Figure 2: FESEM of a) PS, b) PSAW 5 and c) PSAW 20**

### 3. UV- Vis SPECTROSCOPY

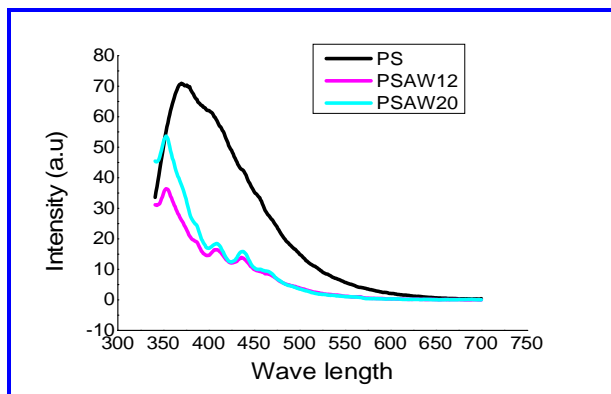
UV- Vis spectroscopy of pure polystyrene and polystyrene/ AgNW composites is shown in fig. 3. The absorption spectrum of PS shows a peak at approximately 250 nm which may be due to isolated phenyl groups of polystyrene. In the composites the peak has shifted to 280 nm which may be due to the interactions between the adjacent phenyl rings (Tong Li *et al.* 1991). This has happened after doping the polystyrene with AgNWs. This may be due to improved connectivity with the increase in dopant concentration of AgNWs in PS matrix.



**Fig. 3: UV- Vis spectroscopy of PS and PSAW composites**

In polystyrene other than peak at 250 nm there is no other peak in the visible region. In PSAW5, PSAW10 and PSAW15 samples there is a peak at 350 nm and a peak at 380 nm. In PSAW12 and PSAW20 both these peaks combined to form a broad peak from approximately 350 nm to 380 nm. These peaks in the composites may be due to transverse surface plasmon resonance of AgNWs in PS matrix. These peaks are due to strong interaction of conduction electrons of silver with the photons of light, oscillating at particular wavelengths, which results in strong absorption properties.

#### Photoluminescent Spectroscopy:



**Fig. 4: Photoluminescence Spectra of PS and PSAW composites**

Fig. 4 shows the photoluminescence spectra of pure polystyrene and its composites which are excited at a wavelength of 320 nm. The photoluminescent spectrum of pure polystyrene shows an emission peak at 369 nm. This peak is due to the production of luminescent matter like styrene, methyl benzonate, double bonds in the main chain of polystyrene. (Toshio Uchihara *et al.* 2010).

In the PL spectra of PSAW composites, several emission bands have been noticed at 350 nm, 410 nm and at 440 nm. The peak at 350 nm may be due to polystyrene. In pure PS the peak has been seen at 369 nm. That peak may have shifted to 350 nm after the introduction of AgNWs in to the polystyrene matrix. This shifting of emission peak to lower wavelengths may be due to the influence of AgNWs on the phenyl group alignment in main chain of polystyrene which was also observed in XRD of the composites.

The emission peaks at 410 nm and 440 nm in the graph of composites can be attributed to photoluminescent radioactive recombination of sp – band electrons with the holes in the valance d band and that have been scattered to Fermi levels.

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